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Development of high throughput evaluation for photocatalyst thin-film

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Abstract

A combinatorial method suitable for accelerating the development of new thin-film photocatalysts was developed. It is constituted by a high throughput evaluation of photocatalytic activity using two-dimensional pH imaging method, synthesis of thin-film libraries using laser molecular beam epitaxy (MBE) technique combined with mask system and analysis using two-dimensional fluorescence X-ray. The principle and details of the high throughput evaluation method were described. Ferric sulfate liquid film was placed on the combinatorially prepared cobalt-doped TiO_2 thin-film library, and then irradiated by visible light. Photo excited electrons reduced ferric ions to ferrous ions. Positive holes oxidized water to oxygen molecules. The resulting increase of proton concentration in the liquid film was measured by two-dimensional pH imaging, indicating the strengthening of photocatalytic activity. As a demonstration of this evaluation method, a library of TiO_2 films doped with cobalt was screened. Doping with cobalt at 5.4–9 atom % made TiO_2 active under visible light irradiation. © 2002 Elsevier Science B.V. All rights reserved.

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Keywords: High throughput evaluation; Photocatalyst; Combinatorial method; pH imaging

1. Introduction

Combinatorial chemistry has been developed for accelerating the discovery of new pharmaceuticals. Its effectiveness for drug discovery has been widely recognized. Expecting that combinatorial method could be effective also for discovery of new catalysts, especially thin-film type catalysts, we tried to develop a combinatorial method suitable for accelerating discovery of new thin-film photocatalysts. Such combinatorial method should consist of three kinds of combinatorial technology. The first is combinatorial synthesis of thin-film libraries. The second is combinatorial analysis of compositions of thin-film libraries. The last is combinatorial or high throughput evaluation of catalyst activity. Combinatorial synthesis is to prepare material libraries with different chemical compositions by single continuous or sequential operation. In the present work, thin-film catalyst libraries were prepared by combinatorial laser molecular beam epitaxy (CLMBE) apparatus that employs the laser MBE technique for thin-film deposition combined with a combinatorial mask system (Matsumoto et al. [1]). Combinatorial analysis was performed by using a two-dimensional fluorescence X-ray. For combinatorial activity evaluation, a two-dimensional pH imaging

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method was used, which is main topic of this paper. Additionally, we explained the principle of two-dimensional pH imaging for evaluating photocatalyst activity, and then introduced an example to indicate how we use this method to evaluate a thin-film system with/without photocatalytic activity under visible light irradiation.

Titanium oxide (TiO_2) absorbs ultra-violet ray (UV). Platinum is known as a catalyst that can activate reactions involving hydrogen or proton. Titanium oxide film spotted with platinum on its surface, $Pt–TiO_2$, can split water photocatalytically, generating hydrogen and oxygen gases, under UV irradiation [2]. However, TiO_2 and $Pt–TiO_2$ do not absorb visible light and hence they do not show any photocatalytic activity under visible light irradiation. To develop a metal–TiO_2 system with photocatalytic activity under visible light irradiation would be useful, since visible light but not UV ray carries major part of solar energy. Our coworkers (Dr. Matsumoto et al.) and we expect that TiO_2 film doped with some transition metals would be photocatalytically active under visible light irradiation. Therefore they combinatorially synthesized libraries of TiO_2 thin-films doped with one of the 12 kinds of transition metals at various concentrations. By preliminary screening using the combinatorial method reported in the following, we found that cobalt among 12 transition metals is most effective to give photocatalytic activity to TiO_2 under visible light. Therefore, from the whole set of libraries, we chose a library, TiO_2 thin-film doped with cobalt at various concentrations, for demonstrating in detail our combinatorial method.

In the following, we will explain the principle of photocatalytic activity evaluation using a two-dimensional pH image sensor. Fig. 1 illustrates the principle of water splitting by photocatalyst. Electrons at the energy level of valence band of semi-conductor such as TiO_2 are excited by photon to the conduction band. The excited electrons move to the surface of semi-conductor, where they reduce protons to hydrogen molecules. Positive holes generated at the valence band accept electrons from hydroxyl anions, generating oxygen molecules and protons. This explanation may be not exact but rather conceptual. If the proton reduction is replaced by some other reductive reaction that consumes excited electrons as shown in Fig. 2, protons are not consumed in the process of reductive reaction while they are generated in the process of
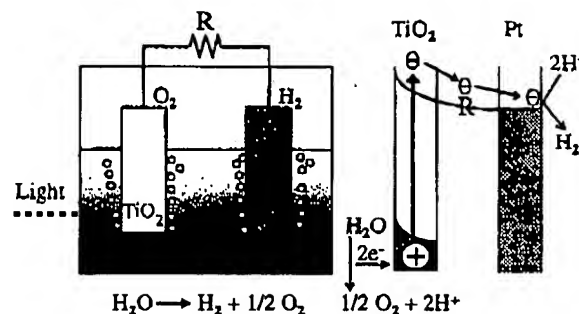

Fig. 1. Principle of photocatalytic water splitting.

oxygen generation. As a result, proton concentration in water increases due to photocatalytic activity. Hence photocatalytic activity can be evaluated by measuring proton concentration or pH in water near the catalyst surface. In the present work, we applied ferric ion reduction to replace the proton reduction. Since the energy of electrons required for reducing ferric ions is less than that for reducing protons to hydrogen molecules, photocatalysts screened by this method may not be able to split water into hydrogen and oxygen. Still this two-dimensional pH image sensing seems to be useful for preliminarily selection of photocatalysts that are active under visible light irradiation.

Hafeman et al. [3] publicized their light addressable potentiometric sensor (LAPS). LAPS is an insulated semi-conductor device that responds to surface potential at an electrolyte–solid interface through the effect of such potential on electric field within the semi-conductor. In case of pH sensor application, protons adsorbed on the surface establish such surface
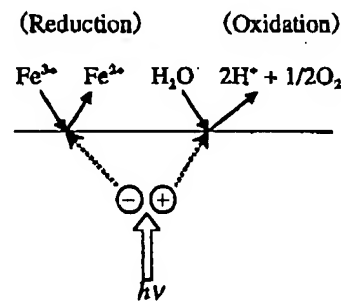

Fig. 2. Replacement of protons by ferric ions in photocatalytic reduction of aqueous solution.
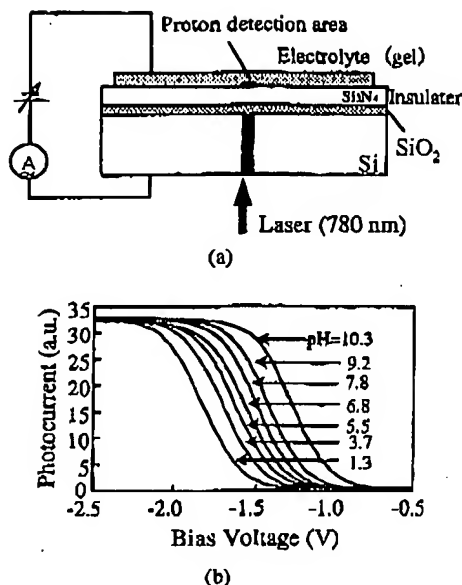
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Fig. 3. Two-dimensional pH measurement of minute area: (a) system (b) dependence of photocurrent intensity on pH and bias voltage.

Fig. 4. Diffusion of protons from the photocatalyst surface to the silicon nitride surface of two-dimensional pH image sensor.

potential. Horiba, an instrument manufacturer in Japan, developed a two-dimensional pH imaging sensor by applying the principle of LAPS. The sensor is composed of silicon substrate, silica thin-film, silicon nitride (Si_3N_4) insulator and agar gel containing electrolyte as shown in Fig. 3a. When laser is spotted, alternating photocurrent is generated. The photocurrent intensity depends not only on the amount of protons adsorbed on the spotted area but also on the used bias voltage as shown in Fig. 3b. The bias voltage is selected as photocurrent changes most sensitively to pH change. For measuring proton amount in solution on the surface of photocatalysts, the photocatalyst sample is placed upside down on the electrolyte gel (Fig. 4). The protons diffuse through the gel and adsorb to the surface of the insulator Si_3N_4.

2. Experimental

2.1. Co-doped TiO_2 thin-film library

Matsumoto and his coworkers prepared the combinatorial libraries of TiO_2 thin-films doped with transition metals at various concentrations illustrated in
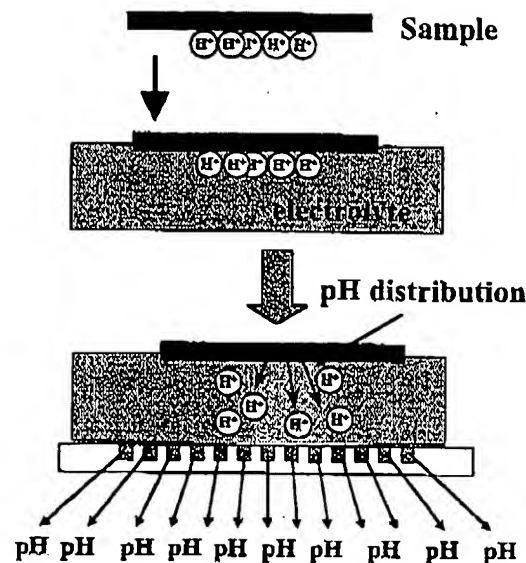
Fig. 5. Among the libraries, we chose cobalt-doped rutile TiO_2 thin-film prepared on substrate Al_2O_3 for combinatorial analysis of compositions and evaluation of photocatalytic activity. The library is a square thin plate of 16 mm × 16 mm divided into 3 × 3 members.

2.2. Combinatorial analysis

Cobalt concentration of each member of the library was measured by two-dimensional fluorescence X-ray analysis (μ-XRF Elemental Analyzers, EAGLE II, EDAX, Tokyo).

2.3. Photocatalytic reaction and evaluation of activity

First, 0.2 μl of 0.01 M ferric sulfate solution was placed on the each member of cobalt-doped TiO_2 thin-film catalyst library. Secondly, the library was irradiated by visible light (>420 nm) for 280 s. Light source was USHIO SPOT-CURE SP-III (250 W) equipped with a filter that cuts off light with wavelength below 420 nm. Thirdly, the library plate was dried at room temperature, inverted and placed on the electrolyte gel of the two-dimensional pH image
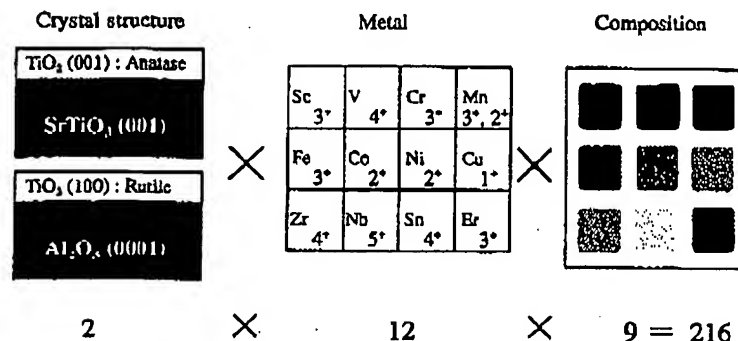
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Fig. 5. Combinatorial synthesis of TiO$_2$ thin-films doped with one of the 12 transition metals at nine concentration levels.

sensor (SCHEM-100, Horiba, Kyoto, Japan). The pH sensor was positioned on the XY stage of SCHEM-100, and the stage moved in X or Y direction by 20 mm at a pitch of 400 μm. Photocurrent was measured at a bias voltage of −1500 mV. Three cycles (180 s/cycle) of measurements were conducted.

3. Results and discussion

3.1. Combinatorial analysis of composition

Red figures in the leftmost picture of Fig. 6 shows cobalt concentration quantified as atom %. The quantitative results indicate that doping of TiO$_2$ films with cobalt at orderly decreasing concentrations was conducted as intended. However, control of absolute cobalt doping concentration may not be easy by CLMBE.

3.2. Combinatorial evaluation of photocatalytic activity

Fig. 6 shows two-dimensional pH image of the library on which photocatalytic reaction was conducted under visible light irradiation. More reddish color represents higher proton concentration (lower pH), and more bluish color shows lower proton concentration (higher pH). Among the library members, numbers 2 and 3, of which cobalt concentrations are 9 and 8.8 atom %, respectively, show the highest photocatalytic activity. The TiO$_2$ films with cobalt concentrations below 4.6 atom % seem to have no significant photocatalytic activity under visible light irradiation. The result of the first or second cycle is more convenient than that of the third cycle to screen photocatalysts with higher activity by a glance, since due to lateral diffusion of protons the image of neighbor members overlapped each other in the third cycle.
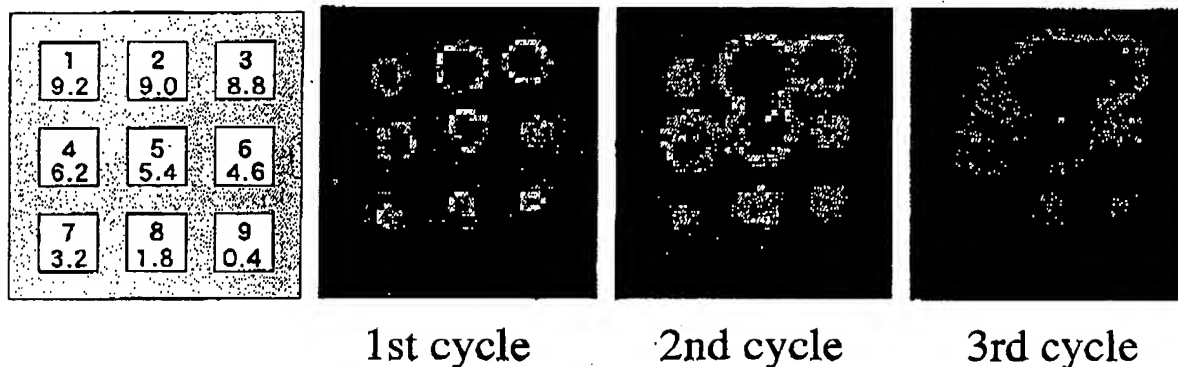

1st cycle   2nd cycle   3rd cycle

Fig. 6. Two-dimensional pH image of photocatalytic activity of cobalt-doped TiO$_2$ thin-film library. Black figures are library member numbers. Red figures are cobalt concentrations (atom %). More reddish color represents lower pH.
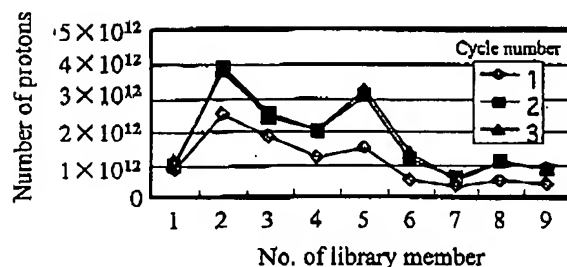
Fig. 7. Amount of protons that diffused from the photocatalyst surface into the electrolyte gel.

For obtaining quantitative data, the proton amount diffused into the gel can be calculated by using the following equation [4]: $N(t) = Ah \sum(10^{-pHx_i,y_i} - 10^{-pHback})$ where pHx_i,y_i, $pHback$, A and h are the pH values at each pixel (X_i,Y_i), background pH value of the agar film (pH 7.4), pixel area (0.16 mm^2) and agar film thickness (0.5 mm), respectively. The pH distribution perpendicular to the sensor was assumed to be zero. The results of calculation are shown in Fig. 7, indicating that the member 2 is the most active, although the members 3 and 5 also exhibit rather high activity.

For more strict comparison, subtraction of proton concentrations of negative control experiment without irradiation from the result of each cycle measurement is necessary, since proton concentration of ferric sulfate solution itself is high (pH 2.2). Another negative control is TiO$_2$ without doping. It is well known that TiO$_2$ itself has no or negligible photocatalytic activity under visible light irradiation. Therefore, if each library includes TiO$_2$ without doping as negative control member in it, then the proton concentration of the negative control member can be subtracted from that of the other members in the same irradiation experiment. When the latter negative control is applied, the former one is unnecessary. For quantifying the number of protons generated by photocatalytic reaction more strictly, some method to prevent the lateral diffusion of protons into the neighbor member area should be developed.

4. Conclusion

A combinatorial method suitable for accelerating the discovery of new thin-film photocatalysts was developed. It is constituted by the two-dimensional pH imaging sensor, synthesis of thin-film libraries using CLMBE, and analysis using two-dimensional fluorescence X-ray. The two-dimensional pH imaging method is convenient for the quick screening of photocatalyst. Researchers can select more active photocatalysts by a glance with this method. The method may not be applicable for the last stage screening of photocatalysts for water splitting, since water splitting needs electrons having potential energy higher than ferric ion reduction does.

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